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<p>(54) Title: <b>DISHWASHING DETERGENT COMPOSITIONS CONTAINING ALKANOLAMINE</b></p> <p>(57) Abstract</p> <p>The present invention relates to detergent compositions containing alkanolamines, preferably triethanolamines, divalent ions, chelants, and amphoteric surfactants. More particularly, the invention is directed to detergent compositions for hand dishwashing which has improved grease removal performance and benefits in sudsing. The detergent compositions of this invention can be in any form, including granular, gel or liquid. Highly preferred embodiments are in liquid form.</p>			

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## DISHWASHING DETERGENT COMPOSITIONS CONTAINING ALKANOLAMINE

Field of the Invention

The present invention relates to detergent compositions containing alkanol amines, preferably triethanol amines (TEA). More particularly, the invention is directed to detergent compositions for hand dishwashing which has improved grease removal performance and benefits in sudsing. The detergents of this invention also have improved low temperature stability properties and dissolution properties, as well as improved grease removal, tough food stain removal, and antibacterial properties. The detergent compositions of this invention can be in any form, including granular, paste, gel or liquid. Highly preferred embodiments are in liquid or gel form.

When formulated into hand dishwashing detergents at a pH of above about 8.0, the alkanol amines became increasingly more effective in combination with Ca or Mg ions and amphoteric surfactants to the extent they provide simultaneous benefits in grease cleaning, sudsing, and mildness.

Background of the Invention

Typical commercial hand dishwashing compositions incorporate divalent ions (Mg or Ca) to ensure adequate grease performance in soft water. However, the presence of divalent ions in formulas containing anionic and additional surfactants (e.g., alkyl dimethyl amine oxide, alkyl ethoxylate, alkanoyl glucose amide, alkyl betaines) leads to slower rates of product mixing with water (and hence poor flash foam), poor rinsing, and poor low temperature stability properties. Moreover, preparation of stable dishwashing detergents containing Ca or Mg is very difficult due to the precipitation issues associated with Ca and Mg as pH becomes more basic.

It has now been determined that the use of alkanolamines, such as triethanolamine (TEA) and/or diethanolamines (DEA), as outlined in detail below, with amphoteric surfactants and Mg or Ca ions in dishcare compositions with pH's ~8.0-10 (as measured as 10% aqueous solution) leads to improved cleaning of tough food stains and removal of grease/oil. Unexpectedly, alkanolamines also improve suds stability in the presence of soils, esp. soils containing fatty acids.

Further, the strong grease removal performance of the combination of alkanolamines as discussed herein allows reduction of Mg or Ca ions from the formulation while maintaining benefits in grease performance.

The alkanolamines of this invention in combination with amphoteric surfactants also provides sensory benefits, such as a "silky" feel to wash liquor and a feeling of "mildness" to the skin. Moreover with the use of alkanolamines, the need for additional buffers are reduced.

It has now been found these benefits are achieved through the use of alkanolamines in combination of Mg or Ca ions and amphoteric in higher pH formulations (~8.0-10) across a broad range of hardness (8 to >1,000 ppm).

#### Background Art

See U.S. Pat. No. 5,376,310; 5,378,409; and 5,369,974.

#### Summary of the Invention

The detergent compositions according to the present invention comprise alkanolamines, such as triethanolamines (TEA) and diethanolamines (DEA), Mg or Ca ions, and amphoteric surfactants. More specifically, the detergents of this invention comprise:

- a) an effective amount of alkanolamines, preferably from selected from TEA, DEA, and mixtures thereof;
- b) a detergents effective amount of amphoteric surfactant;
- c) a detergents effective amount of divalent ions; and
- d) a chelant; said chelant present in a weight ratio of from about 2:1 to about 1:1 of divalent ion to chelant;

wherein the detergent composition has a pH (as measured as 10% aqueous solution) of from about 8.0 to about 12, preferably from about 8.0 to about 10, more preferably from about 8.5 to about 10; still more preferably from about 8.5 to about 9. The preferred chelant is citric acid or citrate.

The preferred weight ratios of amphoteric surfactant to alkanolamine ranges from about 10:1 to about 5:1, more preferably about 10:1 to about 7:1.

The compositions herein utilize from about 0.5% to about 1.5% of available divalent ions, preferably selected from calcium and magnesium.

The detergent will further preferably comprise one or more detergents adjuncts selected from the following: anionic surfactants, nonionic surfactants, cationic surfactants, soil release polymers, dispersants, polysaccharides, abrasives, bactericides, tarnish inhibitors, builders, enzymes, dyes, buffers, antifungal or

mildew control agents, insect repellants, perfumes, hydrotropes, thickeners, processing aids, suds boosters, brighteners, and anti-corrosive aids.

Preferred amphoteric surfactant includes C<sub>12</sub> -C<sub>18</sub> amidopropyl betaines, C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and mixtures thereof.

Anionic surfactants optionally for use herein include linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, methyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl alkoxy carboxylate, alkyl sulfonates, alkyl alkoxy sulfates, sarcosinates, and taurinates. Nonionic surfactants optionally useful herein are selected from the group consisting of alkyl dialkyl amine oxide, alkyl ethoxylate, alkanoyl glucose amide, alkylpolyglucoside, and mixtures thereof.

Moreover, the hand dishwashing detergent composition of this invention can further comprise enzymes preferably selected from the group consisting of protease, lipase, amylase, cellulase, and mixtures thereof. Highly preferred embodiments comprise protease, amylase, and mixtures thereof.

All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

#### Detailed Description of the Invention

**Definitions** - The present detergent compositions comprise an "effective amount" or a "grease removal-improving amount" of individual components defined herein. By an "effective amount" of the alkanolamine herein and adjunct ingredients herein is meant an amount which is sufficient to improve, either directionally or significantly at the 90% confidence level, the performance of the cleaning composition against at least some of the target soils and stains. Thus, in a composition whose targets include certain grease stains, the formulator will use sufficient alkanolamine to at least directionally improve cleaning performance against such stains. Importantly, in a fully-formulated detergent the alkanolamine can be used at levels which provide at least a directional improvement in cleaning performance over a wide variety of soils and stains, as will be seen from the examples presented hereinafter.

As noted, alkanolamine are used herein in detergent compositions in combination with detergents surfactants at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a hand dishwashing composition, such "usage levels" can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the

volume of wash water and the length of time the dishware is contacted with the wash water.

Since the habits and practices of the users of detergent compositions show considerable variation, it is satisfactory to include from about 0.25% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 0.5% to about 6%, by weight, of alkanolamine in such compositions.

In one of its several aspects, this invention provides a means for enhancing the removal of greasy/oily soils by combining alkanolamine of this invention with amphoteric surfactants, chelant and divalent ions. Greasy/oily "everyday" soils are a mixture of triglycerides, lipids, complex polysaccharides, fatty acids, inorganic salts and proteinaceous matter.

Depending on consumer preferences, the compositions herein may be formulated at viscosities of over about 50, preferably over about 100 centipoise, and more preferably from about 100 to about 400 centipoise. For European formulations, the compositions may be formulated at viscosities of up to about 700 centipoise.

Moreover, the superior rate of dissolution achieved herein even allows the formulator to make hand dishwashing detergents, especially compact formulations, at even significantly higher viscosities (e.g., 1,000 centipoise or higher) than conventional formulations while maintaining excellent dissolution and cleaning performance. This has significant potential advantages for making compact products with a higher viscosity that helps denote the "Ultra" concept while maintaining acceptable dissolution. By "compact" or "Ultra" is meant detergent formulations with reduced levels of water compared to conventional liquid detergents. The level of water is less than 50%, preferably less than 30% by weight of the detergent compositions. Said concentrated products provide advantages to the consumer, who has a product which can be used in lower amounts and to the producer, who has lower shipping costs.

Superior grease cleaning and dissolution performance are obtained if the pH of the detergent is maintained in the range of about 8.0 to about 10.

Chelating Agents - The detergent compositions herein contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as chelating agents include ethylenediaminetetra-tates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapro-prionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldi-glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

Amphoteric Surfactants - Ampholytic surfactants are incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Preferred amphoteric include C<sub>12</sub>-C<sub>18</sub> alkyl amido propyl betaines, C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and mixtures thereof.

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued

December 30, 1975 at column 19, line 38 through column 22, line 48 for examples of zwitterionic surfactants.

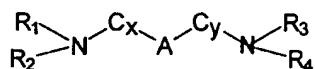
Diamines - Organic diamines useful herein are those in which pK1 and pK2 are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about about 10.75. Preferred materials for performance and supply considerations are 1,3 propane diamine, 1,6 hexane diamine, 1,3 pentane diamine (Dytek EP), 2-methyl 1,5 pentane diamine (Dytek A). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C4 to C8. In general, it is believed that primary diamines are preferred over secondary and tertiary diamines.

Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa". pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability Constants: Volume 2, Amines" by Smith and Martel, Plenum Press, NY and London, 1975. Additional information on pKa's can be obtained from relevant company literature, such as information supplied by Dupont, a supplier of diamines.

As a working definition herein, the pKa of the diamines is specified in an all-aqueous solution at 25°C and for an ionic strength between 0.1 to 0.5 M. The pKa is an equilibrium constant which can change with temperature and ionic strength; thus, values reported in the literature are sometimes not in agreement depending on the measurement method and conditions. To eliminate ambiguity, the relevant conditions and/or references used for pKa's of this invention are as defined herein or in "Critical Stability Constants: Volume 2, Amines". One typical method of measurement is the potentiometric titration of the acid with sodium hydroxide and determination of the pKa by suitable methods as described and referenced in "The Chemist's Ready Reference Handbook" by Shugar and Dean, McGraw Hill, NY, 1990.

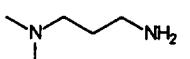
It has been determined that substituents and structural modifications that lower pK1 and pK2 to below about 8.0 are undesirable and cause losses in performance. This can include substitutions that lead to ethoxylated diamines, hydroxy ethyl substituted diamines, diamines with oxygen in the beta (and less so gamma) position to the nitrogen in the spacer group (e.g., Jeffamine EDR 148). In addition, materials based on ethylene diamine are unsuitable.

The diamines useful herein can be defined by the following structure:

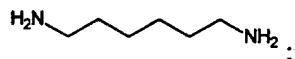


wherein R<sub>1-4</sub> are independently selected from H, methyl, -CH<sub>3</sub>CH<sub>2</sub>, and ethylene oxides; C<sub>x</sub> and C<sub>y</sub> are independently selected from methylene groups or branched alkyl groups where x+y is from about 3 to about 5; and A is optionally present and is selected from electron donating or withdrawing moieties chosen to adjust the diamine pKa's to the desired range.

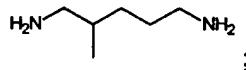
Examples of preferred diamines include the following:



### Dimethyl aminopropyl amine:

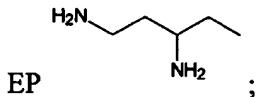


### 1,6-Hexane Diamine:



### 2-methyl 1,5 pentane diamine -

1,3-Pentanediamine, commercially available under the trademark Dytex



### 1-methyl-diaminopropane -

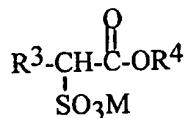
Secondary Surfactants - Secondary detergents can be selected from the group consisting of anionic, nonionics, cationics, zwitterionics, and mixtures thereof. By selecting the type and amount of detergents, along with other adjunct ingredients disclosed herein, the present detergent compositions can be formulated to be used in the context of laundry cleaning or in other different cleaning applications, particularly including dishwashing. The particular surfactants used can therefore vary widely depending upon the particular end-use envisioned. Suitable secondary surfactants are described below.

Anionic Surfactants - An effective amount, typically from about 0.75% to about 90%, preferably about 5% to about 50%, more preferably from about 10 to

about 30%, weight %, of anionic detergents can be an ingredient in the present invention.

One type of anionic surfactant which can be utilized encompasses alkyl ester sulfonates. These are desirable because they can be made with renewable, non-petroleum resources. Preparation of the alkyl ester sulfonate surfactant component can be effected according to known methods disclosed in the technical literature. For instance, linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids can be sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society," 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm, and coconut oils, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprises alkyl ester sulfonate surfactants of the structural formula:



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a soluble salt-forming cation. Suitable salts include metal salts such as sodium, potassium, and lithium salts, and substituted or unsubstituted ammonium salts, such as methyl-, dimethyl-, trimethyl-, and quaternary ammonium cations, e.g. tetramethyl-ammonium and dimethyl piperidinium, and cations derived from alkanolamines, e.g. monoethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>14</sub>-C<sub>16</sub> alkyl.

Alkyl sulfate surfactants are another type of anionic surfactant of importance for use herein. In addition to providing excellent overall cleaning ability when used in combination with polyhydroxy fatty acid amides (see below), including good grease/oil cleaning over a wide range of temperatures, wash concentrations, and wash times, dissolution of alkyl sulfates can be obtained, as well as improved formulability in liquid detergent formulations are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H, Mg, or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperidinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and

mixtures thereof, and the like. Typically, alkyl chains of C<sub>12</sub>-16 are preferred for lower wash temperatures (e.g., below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl alkoxylated sulfate surfactants are another category of useful anionic surfactant. These surfactants are water soluble salts or acids typically of the formula RO(A)<sub>m</sub>SO<sub>3</sub>M wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or hydroxyalkyl, more preferably C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkylamines, e.g. tetraethylamine, tetrapropyl amine, and mixtures thereof. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate, and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium.

Other Anionic Surfactants - Other anionic surfactants useful for detergents can also be included in the compositions hereof. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>9</sub>-C<sub>20</sub> linear alkylbenzenesulphonates, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulphonates, C<sub>8</sub>-C<sub>24</sub> olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>k</sub>CH<sub>2</sub>COO-M<sup>+</sup> wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an

integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants include: alkyl ethoxylate, alkanoyl glucose amide, and mixtures thereof.

Other nonionic surfactants for use herein include:

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol.

Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene

oxide), Neodol<sup>®</sup> 23-6.5 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 6.5 moles of ethylene oxide), Neodol<sup>®</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>®</sup> 45-4 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro<sup>®</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8<sup>®</sup> marketed by Shell Chemical Co. and Genapol UD-080<sup>®</sup> marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic<sup>®</sup> surfactants, marketed by BASF.

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>®</sup> compounds, marketed by BASF.

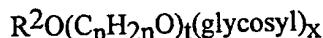
Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about

18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexa-glucosides.

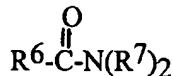
The preferred alkylpolyglycosides have the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms;  $n$  is 2 or 3, preferably 2;  $t$  is from 0 to about 10, preferably 0; and  $x$  is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the

1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:

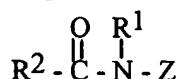


wherein  $\text{R}^6$  is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each  $\text{R}^7$  is selected from the group consisting of hydrogen,  $\text{C}_1\text{-C}_4$  alkyl,  $\text{C}_1\text{-C}_4$  hydroxyalkyl, and  $-(\text{C}^2\text{H}_4\text{O})_x\text{H}$  where  $x$  varies from about 1 to about 3.

Preferred amides are  $\text{C}_8\text{-C}_{20}$  ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

**Polyhydroxy Fatty Acid Amide Surfactant** - The detergent compositions hereof may also contain an effective amount of polyhydroxy fatty acid amide surfactant. By "effective amount" is meant that the formulator of the composition can select an amount of polyhydroxy fatty acid amide to be incorporated into the compositions that will improve the cleaning performance of the detergent composition. In general, for conventional levels, the incorporation of about 1%, by weight, polyhydroxy fatty acid amide will enhance cleaning performance.

The detergent compositions herein will typically comprise about 1% weight basis, polyhydroxy fatty acid amide surfactant, preferably from about 3% to about 30%, of the polyhydroxy fatty acid amide. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein:  $\text{R}^1$  is H,  $\text{C}_1\text{-C}_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably  $\text{C}_1\text{-C}_4$  alkyl, more preferably  $\text{C}_1$  or  $\text{C}_2$  alkyl, most preferably  $\text{C}_1$  alkyl (i.e., methyl); and  $\text{R}^2$  is a  $\text{C}_5\text{-C}_{31}$  hydrocarbyl, preferably straight chain  $\text{C}_7\text{-C}_{19}$  alkyl or alkenyl, more preferably straight chain  $\text{C}_9\text{-C}_{17}$  alkyl or alkenyl, most preferably straight chain  $\text{C}_{11}\text{-C}_{15}$  alkyl or alkenyl, or mixtures thereof; and  $\text{Z}$  is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof.  $\text{Z}$  preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably  $\text{Z}$  will be a glycetyl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the

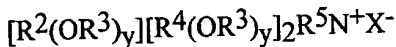
individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of  $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$ , and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ . R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2\text{-CO-N}^<$  can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

Cationic Surfactants - Cationic detergents can also be included in detergent compositions of the present invention. Cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein  $\text{R}^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $\text{R}^3$  is selected from the group consisting of  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , and mixtures thereof; each  $\text{R}^4$  is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl, ring structures formed by joining the two  $\text{R}^4$  groups, - $\text{CH}_2\text{CHOHCHOHCOR}^6\text{CHOH-CH}_2\text{OH}$  wherein  $\text{R}^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is

not O; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Builder - The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylene-diamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R-CH(COOH)CH<sub>2</sub>(COOH) wherein R is C10-20 alkyl or alkenyl, preferably C12-16, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate 2-dodeceny succinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Other preferred builder system for liquid compositions is based on dodecetyl succinic acid and citric acid.

Detergency builder salts are normally included in amounts of from 3% to 50% by weight of the composition preferably from 5% to 30% and most usually from 5% to 25% by weight.

Optional Detergent Ingredients: - Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases,

arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase.

Cellulases - the cellulases usable in the present invention include both bacterial or fungal cellulase. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Proteolytic Enzyme - The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. The proteases for use in the detergent compositions herein include (but are not limited to) trypsin, subtilisin, chymotrypsin and elastase-type proteases. Preferred for use herein are subtilisin-type proteolytic enzymes. Particularly preferred is bacterial serine proteolytic enzyme obtained from *Bacillus subtilis* and/or *Bacillus licheniformis*.

Suitable proteolytic enzymes include Novo Industri A/S Alcalase® (preferred), Esperase®, Savinase® (Copenhagen, Denmark), Gist-brocades' Maxatase®, Maxacal® and Maxapem 15® (protein engineered Maxacal®) (Delft, Netherlands), and subtilisin BPN and BPN' (preferred), which are commercially available.

Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those made by Genencor International, Inc. (San Francisco, California) which are described in European Patent 251,446B, granted December 28, 1994 (particularly pages 17, 24 and 98) and which are also called herein "Protease B". U.S. Patent 5,030,378, Venegas, issued July 9, 1991, refers to a modified bacterial serine proteolytic enzyme (Genencor International) which is called "Protease A" herein (same as BPN'). In particular see columns 2 and 3 of U.S. Patent 5,030,378 for a complete description, including amino sequence, of Protease A and its variants. Other proteases are sold under the tradenames: Primase, Durazym, Opticlean and Optimase. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase® (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred.

Of particular interest for use herein are the proteases described in U.S. Patent No. 5,470,733.

Also proteases described in our co-pending application USSN 08/136,797 can be included in the detergent composition of the invention. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Another preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International (A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, filed October 13, 1994).

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Lipase - suitable lipase enzymes include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a

positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as M1 Lipase® and Lipomax® (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826. (See also patent application WO 92/05249 viz. wherein the native lipase ex *Humicola lanuginosa* aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the *Humicola lanuginosa* strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for washing products. It is available from Novo Nordisk under the tradename Lipolase® and Lipolase Ultra®, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

Lipase enzyme is incorporated into the composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Amylase - Amylases ( $\alpha$  and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl<sup>®</sup> (Novo Nordisk), Fungamyl<sup>®</sup> and BAN<sup>®</sup> (Novo Nordisk). The enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Amylase enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Amylase enzymes also include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. Other specific amylase enzymes for use in the detergent compositions of the present invention therefore include :

- (a)  $\alpha$ -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay. Such Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay is described at pages 9-10, WO95/26397.
- (b)  $\alpha$ -amylases according (a) comprising the amino sequence shown in the SEQ ID listings in the above cited reference. or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown in the SEQ ID listing.
- (c)  $\alpha$ -amylases according (a) comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

- (d)  $\alpha$ -amylases according (a-c) wherein the  $\alpha$ -amylase is obtainable from an alkalophilic Bacillus species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a Bacillus strain but also an amylase encoded by a DNA sequence isolated from such a Bacillus strain and produced in an host organism transformed with said DNA sequence.

(e)  $\alpha$ -amylase showing positive immunological cross-reactivity with antibodies raised against an  $\alpha$ -amylase having an amino acid sequence corresponding respectively to those  $\alpha$ -amylases in (a-d).

(f) Variants of the following parent  $\alpha$ -amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those  $\alpha$ -amylases in (a-e), or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an  $\alpha$ -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an  $\alpha$ -amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent  $\alpha$ -amylase has been deleted; and/or
2. at least one amino acid residue of said parent  $\alpha$ -amylase has been replaced by a different amino acid residue; and/or
3. at least one amino acid residue has been inserted relative to said parent  $\alpha$ -amylase;

said variant having an  $\alpha$ -amylase activity and exhibiting at least one of the following properties relative to said parent  $\alpha$ -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or  $\alpha$ -amylolytic activity at neutral to relatively high pH values, increased  $\alpha$ -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for  $\alpha$ -amylase variant to the pH of the medium.

Said variants are described in the patent application PCT/DK96/00056.

Other amylases suitable herein include, for example,  $\alpha$ -amylases described in GB 1,296,839 to Novo; RAPIDASE<sup>®</sup>, International Bio-Synthetics, Inc. and TERMAMYL<sup>®</sup>, Novo. FUNGAMYL<sup>®</sup> from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents such as automatic dishwashing types, especially improved oxidative stability as measured against a reference-point of TERMAMYL<sup>®</sup> in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a

minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetyl ethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus*  $\alpha$ -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple

mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Enzyme Stabilizing System - The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergents enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions, for example automatic dishwashing compositions, may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during dish- or fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetra-methylnaphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecenyI propionate; tricyclodecenyI acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin;

para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-naphthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecanyl acetate; and tricyclodecanyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent performance by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG), propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Additionally, polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear,

branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without of course forming a densely crosslinked overall structure.

Suitable SRA's include products as described in U.S. 4,968,451; U.S. 4,711,730; U.S. 4,721,580; U.S. 4,702,857; U.S. 4,877,896; U.S. 3,959,230; U.S. 3,893,929; U.S. 4,000,093; EP Appl. 0 219 048; U.S. 5,415,807; U.S. 4,201,824; U.S. 4,240,918; U.S. 4,525,524; U.S. 4,201,824; U.S. 4,579,681; EP 279,134A; EP 457,205; DE 2,335,044; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; U.S. 4,877,896; U.S. 4,968,451; U.S. 4,702,857; U.S. Appl. 08/545,351; and U.S. Appl. 08/355,938. Commercially available examples include SOKALAN HP-22, available from BASF, Germany; ZELCON 5126 from Dupont; and MILEASE T from ICI.

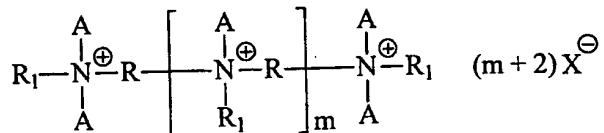
Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Another polymer dispersant form use herein includes polyethoxylated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common polyalkyleneamine (PAA) is tetrabutylbenzenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and

teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

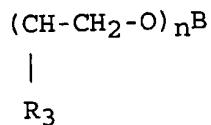
Polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Additionally, certain alkoxylated (especially ethoxylated) quaternary polyamine dispersants are useful herein as dispersants. The alkoxylated quaternary polyamine dispersants which can be used in the present invention are of the general formula:



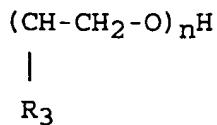
where R is selected from linear or branched C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH<sub>2</sub>]- and -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O-[(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>]- where q is from about 1 to about 100. If present, Each R<sub>1</sub> is independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, or A. R<sub>1</sub> may be absent on some nitrogens; however, at least three nitrogens must be quaternized.

A is of the formula:



where R<sub>3</sub> is selected from H or C<sub>1</sub>-C<sub>3</sub> alkyl, n is from about 5 to about 100 and B is selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl, acetyl, or benzoyl; m is from about 0 to about 4, and X is a water soluble anion.

In preferred embodiments, R is selected from C<sub>4</sub> to C<sub>8</sub> alkylene, R<sub>1</sub> is selected from C<sub>1</sub>-C<sub>2</sub> alkyl or C<sub>2</sub>-C<sub>3</sub> hydroxyalkyl, and A is:



where R<sub>3</sub> is selected from H or methyl, and n is from about 10 to about 50; and m is 1.

In another preferred embodiment R is linear or branched C<sub>6</sub>, R<sub>1</sub> is methyl, R<sub>3</sub> is H, and n is from about 20 to about 50, and m is 1.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized following the methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphtho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active

ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C<sub>10</sub>-C<sub>16</sub> alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C<sub>10</sub>-C<sub>14</sub> monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous.

Various detergents ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detergents ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergents ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detergents function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C<sub>13</sub>-15 ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

An example of the procedure for making liquid detergent compositions herein is as follows: - To the free water, citrate and MgCl<sub>2</sub> are added and dissolved. To this solution amine oxide, betaine, ethanol, hydrotrope and nonionic surfactant are added. If free water isn't available, the MgCl<sub>2</sub> and citrate are added to the above

mix then stirred until dissolved. At this point, maleic acid is added then followed by the alkanolamine. AExS is added last.

#### Non-Aqueous Liquid Detergents

The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate detergents ingredients (e.g., bleaching agents, as disclosed hereinabove) stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

The compositions of this invention can be used to form aqueous washing solutions for use hand dishwashing. Generally, an effective amount of such compositions is added to water to form such aqueous cleaning or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

In the following Examples all levels are quoted as % by weight of the composition.

EXAMPLE I

The following liquid detergent compositions are made :

	A	B	C	D
pH 10%	9	8.5	8.5	9
AE1S	0	28	25	0
AE2.2S	30	0	0	24
Amine Oxide	8	5	7	8
Betaine	3	3	1	0
Polyhydroxy fatty acid amide (C14)	0	4.5	0	0
AE nonionic	2	3	4	3
Triethanolamine	1	5	7	6
Mg <sup>++</sup> (as MgCl <sub>2</sub> )	0.6	0.65	0.65	0.6
Citric Acid	0.5	0.5	0.5	0.5
Balance (water, dye, ethanol, perfume, etc.)	100	100	100	100

	E	F	G
pH 10%	9.3	8.5	9
AE1.4S	0	18	14
Paraffin Sulfonate	20	0	0
Linear Alkyl Benzene Sulfonate	5	15	10
Betaine	3	1	0
Polyhydroxy fatty acid amide (C12)	2	0	0
AE nonionic	2	0	10
Alkylamine oxide	12	11	10
Triethanolamine	4	5	6
Mg <sup>++</sup> (as MgCl <sub>2</sub> )	1	0.6	0.6
Citric Acid	0.75	0.5	0.5
Protease	0.01	0	0.05
Amylase	0	0.05	0.05
Hydrotrope	5	5	5
Balance (water, dye, perfume, etc.)	to 100	to 100	to 100

The amylase is selected from: Termamyl®; Fungamyl®; Duramyl®; and BAN®.

The lipase is selected from: Amano-P; M1 Lipase®; Lipomax®; Lipolase®; D96L - lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826; and the *Humicola lanuginosa* strain DSM 4106.

The protease is selected from: Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®; and Optimase®, and Alcalase ®.

Hydrotropes can be selected from cumene, xylene, and sulfonates.

#### EXAMPLE II

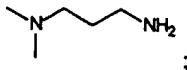
The following granular detergent compositions are made :

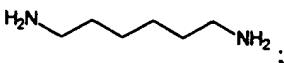
Ingredient	Wt %	Wt %
Linear alkylbenzenesulfonate	30	27
Sodium tripolyphosphate	2	5
Sodium silicate (ratio 2.35)	10	15
Sodium sulfate	40	47
Perfume	0.5	0.5
Triethanolamine	5	2
Moisture	balance	balance

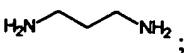
WHAT IS CLAIMED IS:

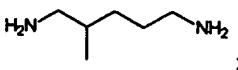
1. A detergent composition suitable for use in hand dishwashing, said composition characterizing:
  - a) an effective amount of alkanolamine;
  - b) a detergents effective amount of amphoteric surfactant;
  - c) a detergents effective amount of divalent ions; and
  - d) a chelant; said chelant present in a weight ratio of from 2:1 to 1:1 of divalent ion to chelant;wherein the detergent composition has a pH (as measured as 10% aqueous solution) of from 8.0 to 12.
2. A hand dishwashing detergent composition according to Claim 1 wherein said amine is triethanolamine.
3. A hand dishwashing detergent composition according to Claim 2 wherein the weight ratio of amphoteric surfactant to triethanolamine is from 10:1 to 5:1.
4. A hand dishwashing detergent composition according to Claim 1 wherein said amphoteric surfactant is selected from the group consisting of C<sub>12</sub> -C<sub>18</sub> alkylamidopropyl betaines, C<sub>12</sub>-C<sub>18</sub> betaines, sulfobetaines, C<sub>10</sub>-C<sub>18</sub> amine oxides, and mixtures thereof.
5. A hand dishwashing detergent composition according to Claim 4 further characterizing one or more detergents adjuncts selected from the following: anionic surfactant, nonionic surfactants, cationic surfactants, diamines, soil release polymers, dispersants, polysaccharides, abrasives, bactericides, tarnish inhibitors, builders, enzymes, dyes, perfumes, thickeners, hydrotropes, processing aids, suds boosters, buffers, antifungal or mildew control agents, insect repellants, brighteners, and anti-corrosive aids.
6. A hand dishwashing detergent composition according to Claim 5 characterizing anionic surfactant selected from the group consisting of linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, methyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl alkoxy carboxylate, alkyl sulfonates, alkyl alkoxy sulfates, sarcosinates, taurinates, and mixtures thereof.

7. A hand dishwashing detergent composition according to Claim 5 characterizing nonionic surfactants selected from the group consisting of alkyl dialkyl amine oxide, alkyl ethoxylate, alkanoyl glucose amide, alkyl polyglucoside, and mixtures thereof.
8. A hand dishwashing detergent composition according to Claim 5 characterizing enzymes selected from the group consisting of protease, lipase, amylase, cellulase, and mixtures thereof.
9. A hand dishwashing detergent composition according to Claim 8 wherein said enzyme is selected from the group consisting of protease, amylase, and mixtures thereof.
10. A hand dishwashing detergent composition according to Claim 4 characterizing diamines selected from the group consisting of:

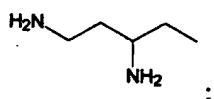
dimethyl aminopropyl amine:  ;

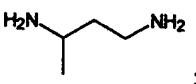
1,6-hexane diamine:  ;

1,3 propane diamine -  ;

2-methyl 1,5 pentane diamine -  ;

1,3-Pentanediamine, commercially available under the tradename Dytex EP-

 ;

1-methyl-diaminopropane -  ;

and mixtures thereof.

11. A hand dishwashing detergent composition according to Claim 1 wherein said composition has a pH of from 8.2 to 10.
12. A hand dishwashing detergent composition according to Claim 1 in liquid form.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/22684

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C11D3/30 C11D3/02 C11D1/94 C11D1/90

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 20028 A (PROCTER & GAMBLE) 27 July 1995 see claims; examples 2E, ,2F, ,4 ----	1-9,11, 12
A	WO 92 08777 A (PROCTER & GAMBLE) 29 May 1992 cited in the application see claims; examples 4-6 ----	1-9,11, 12
A	WO 94 05769 A (PROCTER & GAMBLE) 17 March 1994 see claims; examples 3,4 ----	1-9,11, 12
A	EP 0 232 092 A (GOLDMAN ROBERT ET AL.) 12 August 1987 see page 3, line 19 – page 4, line 16; claims 1-9 ----	1,2,10 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

<sup>a</sup> Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search

Date of mailing of the international search report

2 April 1998

24/04/1998

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/22684

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 269 974 A (OFOSU-ASANTE KOFI) 14 December 1993 see claims -----	1, 4, 11, 12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 97/22684

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9520028 A	27-07-95	NONE		
WO 9208777 A	29-05-92	AT 149561 T	15-03-97	
		AU 9063991 A	11-06-92	
		CA 2055045 A,C	17-05-92	
		CN 1062371 A	01-07-92	
		CZ 9300873 A	13-07-94	
		DE 69125022 D	10-04-97	
		DE 69125022 T	25-09-97	
		EP 0557426 A	01-09-93	
		ES 2101078 T	01-07-97	
		FI 932199 A	14-05-93	
		HU 64782 A	28-02-94	
		JP 6502884 T	31-03-94	
		MX 9102078 A	01-06-92	
		SK 48093 A	12-01-94	
		TR 26532 A	15-03-95	
		US 5378409 A	03-01-95	
		CA 2055048 A,C	17-05-92	
		US 5376310 A	27-12-94	
WO 9405769 A	17-03-94	CA 2143328 A	17-03-94	
		CN 1088251 A	22-06-94	
		EP 0658191 A	21-06-95	
		MX 9305354 A	30-06-94	
EP 0232092 A	12-08-87	AU 590043 B	26-10-89	
		AU 6802687 A	30-07-87	
		JP 1062486 A	08-03-89	
US 5269974 A	14-12-93	CN 1086843 A	18-05-94	
		EP 0658184 A	21-06-95	
		MX 9305356 A	31-03-94	
		WO 9405752 A	17-03-94	